

## SECOND MARKED SPECIFICATION

**Iron-Chromium-Aluminium Alloy****BACKGROUND**

5

**Field of the Invention**

The invention relates to an iron-chromium-aluminium alloy having good oxidation resistance.

10 **Description of Related Art**

Although the catalytic converter is the rule in four-stroke-engines today, the development of catalytic converters for Diesel and two-stroke engines is still in its beginnings. In four-stroke-engines, alloys are used which are similar to those described in EP-A 0387 670: with (in % by weight) 20-25% Cr, 5-8 % Al, max. 0.01 % P, max. 0.01 % Mg, max. 0.5 % Mn, max. 0.005 % S, residual iron and unavoidable impurities and, if required, alloying elements, such as 0.03 - 0.08 % Y, 0.004 - 0.008% N, 0.02 - 0.04 %C, 0.035 - 0.07 % Ti, 0.035 - 0.07 % Zr. Since production by traditional methods, namely conventional pouring of the alloy and subsequent hot and cold deformation, is very difficult where aluminium contents of below 6% by weight are concerned and in cases of higher aluminium contents is no longer workable in large-scale productions, alternative production methods have been developed.

U.S. Patent No. 5,366,139, for instance, discloses a method whereby foils of iron-chromium-aluminium alloys are produced by way of suitable iron-chromium steel being coated on both sides with aluminium or aluminium alloys by way of roll cladding. This composite metal is processed exclusively by cold deformation and is subjected to diffusion annealing to produce a homogeneous structure.

A further method whereby the coating is achieved by way of hot dip aluminizing is disclosed in DE-A 198 34 552. The latter foil has the following chemical composition (all details in %

## SECOND MARKED SPECIFICATION

by weight): 18 - 25 % Cr, 4 - 10 % Al, 0.03 - 0.08 % Y, max. 0.01 % Ti, 0.01 - 0.05 % Zr, 0.01 - 0.05 % Hf, 0.5 - 1.5 % Si, residual iron and method-associated impurities. Foils fabricated with this alloy were to date used in four-stroke-combustion engines.

**5 BRIEF SUMMARY OF THE INVENTION**

It is the object of the present invention to produce an alloy for applications in the temperature range of 250°C to 1000°C having an adequate oxidation resistance which is also achievable in large scale productions.

10

The solution to the task set is provided by an iron-chromium-aluminium alloy having good oxidation resistance, with (in % by weight) 2.5 to 5.0% Al and 10 to 25 % Cr and 0.05-0.8 % Si as well as additions of > 0.01 to 0.1 % Y and/or > 0.01 to 0.1 % Hf and/or > 0.01 to 0.2% Zr and/or > 0.01 to 0.2% Cerium mischmetal (Ce, La, Nd) (i.e., at least two of Ce, La, or Nd) as well as production-associated impurities.

15

A preferred iron-chromium-aluminium alloy having good oxidation resistance has the following composition (in % by weight): 2.5 - 5% Al and 13 to 21% Cr as well as alternative additions of:

20

- > 0.01 to 0.1 % Y and > 0.01 to 0.1 % Hf;
- > 0.01 % to 0.1 % Y and > 0.01 to 0.1 % Hf and > 0.01 % to 0.2 % Zr;
- > 0.01 to 0.2 % Cerium mischmetal (Ce, La, Nd);
- > 0.01 to 0.2 % Zr and > 0.01 to 0.2% Cerium mischmetal (Ce, La, Nd)

25

as well as production-associated impurities.

30

Surprisingly, it has been found that, in Diesel engines and two-stroke engines, aluminium contents above 5 % are not required. 2.5 to 5.0 % by weight are quite sufficient to guarantee an adequate oxidation resistance in the temperature range of 250°C to 1000°C which is of

## SECOND MARKED SPECIFICATION

interest in this regard, as the examples presented below will show. Indispensable in this situation are the additions of reactive elements to guarantee the oxidation resistance.

Particularly proven are 0.01 - 0.1 % Y and/or 0.01 - 0.1 % Hf, where, in the presence of both elements, the sum of both these elements must not exceed 0.15 % by weight, because at this  
5 level the positive effect of the oxidation resistance will be reversed to a negative. However, also by adding other oxygen-affine reactive elements, such as for instance Zr, Cerium mischmetal and La, positive effects can be achieved in relation to the oxidation resistance of the alloy.

10 One method for the fabrication of semi-finished articles from this alloy is characterised in that the semi-finished article following melting of the alloy by way of ingot casting or continuous casting as well as hot and cold deformation may be required to undergo one (or more) intermediate annealing processes.

15 Advantageous embodiments of the method are described in the disclosure.

The production of a foil of 50µm or even 20µm thickness is possible in the conventional manner in such compositions. The slabs can even be produced by way of the particularly inexpensive continuous casting process which in the presence of higher aluminium contents  
20 is, as a rule, connected with high losses.

Preferred applications for this alloy are:

- 25 - components in exhaust systems of Diesel engines in vessels, Diesel engines and two-stroke engines of motor vehicles (cars, trucks) or motorbikes;
- substrate foils in metallic catalytic converters of Diesel engines and two-stroke engines;
- 30 - components in Diesel engine glow plugs;

**SECOND MARKED SPECIFICATION**

- knitted metal fabrics and mats for exhaust cleaning systems used in for instance motorcycles, brush cutters, lawn mowers and power saws;
- 5     - components for exhaust cleaning systems for fuel cells;
- spraying wires for surface coatings of components employed in exhaust systems of diesel and two-stroke systems;
- 10    - heating conductors or resistance materials for electrical preheating of exhaust cleaning systems in Diesel and two-stroke systems.

The subject of the invention is described in greater detail in the following examples.

**15   DETAILED DESCRIPTION**

(Aluchrom ISE, Hf3 and Hf4 represent comparative alloys and Aluchrom Hf1 and Hf2 are the subject of the present invention).

## SECOND MARKED SPECIFICATION

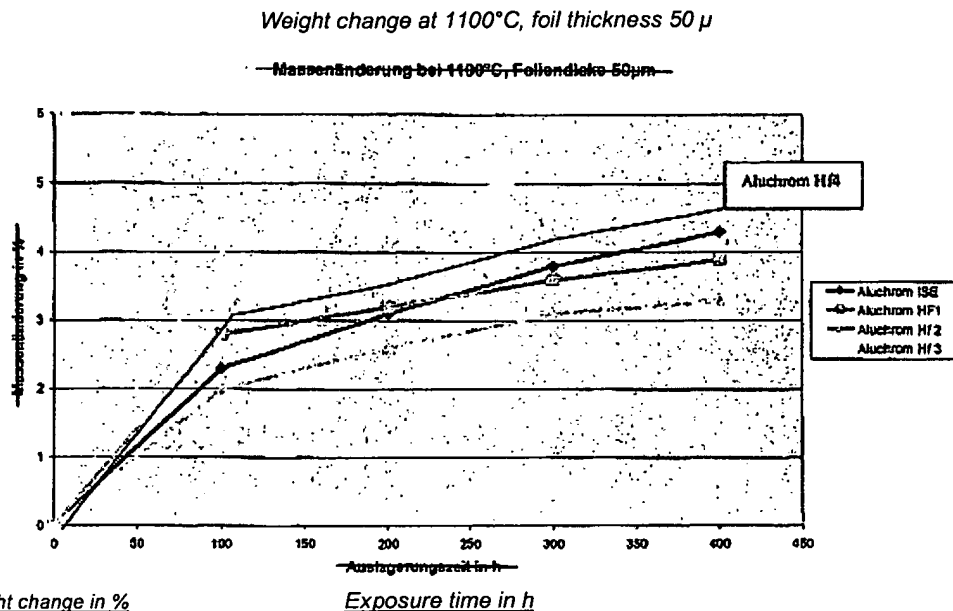
## Chemical compositions

<b>Element/ Masse-% Mass %</b>	<b>Aluchrom ISE</b>	<b>Aluchrom Hf 1</b>	<b>Aluchrom Hf 2</b>	<b>Aluchrom Hf 3</b>	<b>Aluchrom Hf 4</b>
Cr	20,45	17,25	18,20	21,05	20,15
NI	0,19	0,14	0,16	0,17	0,16
Mn	0,25	0,28	0,15	0,11	0,21
SI	0,43	0,54	0,29	0,30	0,22
TI	0,01	<0,01	<0,01	<0,01	0,01
Cu	0,03	0,05	0,02	0,03	0,07
S	0,002	0,002	0,002	0,002	0,002
P	0,011	0,009	0,013	0,009	0,012
Al	5,27	2,78	3,30	5,36	5,70
Mg	0,008	0,004	0,009	0,009	0,009
Zr	0,003	0,05	0,01	0,02	0,05
V	0,04	0,05	0,03	0,04	0,03
C	0,006	0,032	0,023	0,051	0,023
N	0,004	0,005	0,004	0,002	0,005
Hf	--	0,04	0,05	0,03	0,05
Y Cer MM (Ce, LA, Nd)	-- 0,015	0,03 --	0,05 --	<0,01 --	0,06

- 5 The examples in accordance with the invention were produced by melting in the electric arc furnace, continuous casting or ingot casting, hot rolling to a thickness of about 3mm, with intermediate annealing at end thicknesses of 0.02 to 0.05 and cold rolling on a 20 roller scaffold.

## SECOND MARKED SPECIFICATION

## Oxidation test



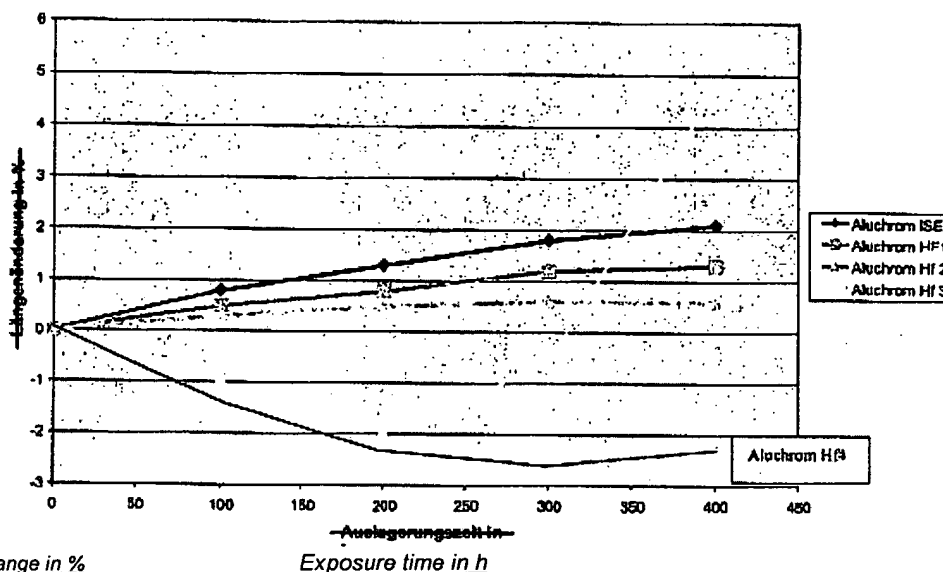
5    ↑ Weight change in %  
      ↑ Exposure time in [h]  
      Linear deformation in %

As the examples show, besides the Al content, the exact tuning of the oxygen affine reactive  
 10 elements is of predominant importance. For instance, the alloys according to the present  
 invention, Aluchrom Hf1 and Aluchrom Hf2, in spite of their comparatively low Al-content  
 of around 3%, show an extremely good oxidation resistance, which is similar to the  
 comparative alloys Aluchrom ISE and Aluchrom Hf4. By comparison, Aluchrom Hf3, in  
 spite of its high Al- content of 5.36%, has lower values which can be attributed to the Y  
 15 content being too low. In this instance therefore additions of Y or Cerium mischmetal result in  
 a markedly improved oxidation resistance. (compare Aluchrom ISE and Aluchrom Hf4).

A further important aspect for the construction of metallic catalytic converter substrates for  
 Diesel engines and two-stroke engines is the dimensional stability of the foil during the useful  
 20 life of the foil. A respective characteristic feature in this regard is the linear deformation  
 which should, if possible, not exceed 4 %.

## SECOND MARKED SPECIFICATION

## Dimensional Stability

Linear deformation at 1100°C, 50  $\mu$  foil thickness~~Längenänderung bei 1100°C, 50  $\mu$ m Folienstärke~~

5

↑ Weight change in %

↑ Exposure time in [h]

Linear deformation in %

- 10 This also shows that the alloys in accordance with the present invention, Aluchrom Hf1 and Aluchrom Hf2, having an Al content of around 3 %, achieve a dimensional stability of < 4% as do the comparative alloys Aluchrom ISE and Aluchrom Hf4 having an Al content of > 5%. Also in this case, in spite of their comparatively high Al content of 5.36 % but too low a Y content, the comparative alloy Aluchrom Hf3 does not meet the requirements, since the linear
- 15 deformation after 400 h, being about 5 %, is clearly too great.

Thus it is surprisingly found that with a suitable tuning of the oxygen-affine reactive elements, even where Al contents clearly below 5 % are present, a dimensional stability necessary for the production of metallic catalytic converters can be achieved.

20

**SECOND MARKED SPECIFICATION**

A cost-effective production, based on the comparatively low Al contents, by way of ingot casting, continuous casting or even strip casting whilst observing the application-specific parameters is thus achieved.

## SECOND SUBSTITUTE SPECIFICATION

**Iron-Chromium-Aluminium Alloy****BACKGROUND**

5

**Field of the Invention**

The invention relates to an iron-chromium-aluminium alloy having good oxidation resistance.

10 **Description of Related Art**

Although the catalytic converter is the rule in four-stroke-engines today, the development of catalytic converters for Diesel and two-stroke engines is still in its beginnings. In four-stroke-engines, alloys are used which are similar to those described in EP-A 0387 670: with (in % by weight) 20-25% Cr, 5-8 % Al, max. 0.01 % P, max. 0.01 % Mg, max. 0.5 % Mn, max. 0.005 % S, residual iron and unavoidable impurities and, if required, alloying elements, such as 0.03 - 0.08 % Y, 0.004 - 0.008% N, 0.02 - 0.04 %C, 0.035 - 0.07 % Ti, 0.035 - 0.07 % Zr. Since production by traditional methods, namely conventional pouring of the alloy and subsequent hot and cold deformation, is very difficult where aluminium contents of below 6% by weight are concerned and in cases of higher aluminium contents is no longer workable in large-scale productions, alternative production methods have been developed.

U.S. Patent No. 5,366,139, for instance, discloses a method whereby foils of iron-chromium-aluminium alloys are produced by way of suitable iron-chromium steel being coated on both sides with aluminium or aluminium alloys by way of roll cladding. This composite metal is processed exclusively by cold deformation and is subjected to diffusion annealing to produce a homogeneous structure.

A further method whereby the coating is achieved by way of hot dip aluminizing is disclosed in DE-A 198 34 552. The latter foil has the following chemical composition (all details in %

## SECOND SUBSTITUTE SPECIFICATION

by weight): 18 - 25 % Cr, 4 - 10 % Al, 0.03 - 0.08 % Y, max. 0.01 % Ti, 0.01 - 0.05 % Zr, 0.01 - 0.05 % Hf, 0.5 - 1.5 % Si, residual iron and method-associated impurities. Foils fabricated with this alloy were to date used in four-stroke-combustion engines.

5    **BRIEF SUMMARY OF THE INVENTION**

It is the object of the present invention to produce an alloy for applications in the temperature range of 250°C to 1000°C having an adequate oxidation resistance which is also achievable in large scale productions.

10

The solution to the task set is provided by an iron-chromium-aluminium alloy having good oxidation resistance, with (in % by weight) 2.5 to 5.0% Al and 10 to 25 % Cr and 0.05-0.8 % Si as well as additions of > 0.01 to 0.1 % Y and/or > 0.01 to 0.1 % Hf and/or > 0.01 to 0.2% Zr and/or > 0.01 to 0.2% Cerium mischmetal (Ce, La, Nd) (i.e., at least two of Ce, La, or Nd) as well as production-associated impurities.

15

A preferred iron-chromium-aluminium alloy having good oxidation resistance has the following composition (in % by weight): 2.5 - 5% Al and 13 to 21% Cr as well as alternative additions of:

20

- > 0.01 to 0.1 % Y and > 0.01 to 0.1 % Hf;
- > 0.01 % to 0.1 % Y and > 0.01 to 0.1 % Hf and > 0.01 % to 0.2 % Zr;
- > 0.01 to 0.2 % Cerium mischmetal (Ce, La, Nd);
- > 0.01 to 0.2 % Zr and > 0.01 to 0.2% Cerium mischmetal (Ce, La, Nd)

25

as well as production-associated impurities.

30

Surprisingly, it has been found that, in Diesel engines and two-stroke engines, aluminium contents above 5 % are not required. 2.5 to 5.0 % by weight are quite sufficient to guarantee an adequate oxidation resistance in the temperature range of 250°C to 1000°C which is of

## SECOND SUBSTITUTE SPECIFICATION

interest in this regard, as the examples presented below will show. Indispensable in this situation are the additions of reactive elements to guarantee the oxidation resistance.

Particularly proven are 0.01 - 0.1 % Y and/or 0.01 - 0.1 % Hf, where, in the presence of both elements, the sum of both these elements must not exceed 0.15 % by weight, because at this  
5 level the positive effect of the oxidation resistance will be reversed to a negative. However, also by adding other oxygen-affine reactive elements, such as for instance Zr, Cerium mischmetal and La, positive effects can be achieved in relation to the oxidation resistance of the alloy.

10 One method for the fabrication of semi-finished articles from this alloy is characterised in that the semi-finished article following melting of the alloy by way of ingot casting or continuous casting as well as hot and cold deformation may be required to undergo one (or more) intermediate annealing processes.

15 Advantageous embodiments of the method are described in the disclosure.

The production of a foil of 50µm or even 20µm thickness is possible in the conventional manner in such compositions. The slabs can even be produced by way of the particularly inexpensive continuous casting process which in the presence of higher aluminium contents  
20 is, as a rule, connected with high losses.

Preferred applications for this alloy are:

- 25 - components in exhaust systems of Diesel engines in vessels, Diesel engines and two-stroke engines of motor vehicles (cars, trucks) or motorbikes;
- substrate foils in metallic catalytic converters of Diesel engines and two-stroke engines;
- 30 - components in Diesel engine glow plugs;

## SECOND SUBSTITUTE SPECIFICATION

- knitted metal fabrics and mats for exhaust cleaning systems used in for instance motorcycles, brush cutters, lawn mowers and power saws;
- 5     - components for exhaust cleaning systems for fuel cells;
- spraying wires for surface coatings of components employed in exhaust systems of diesel and two-stroke systems;
- 10    - heating conductors or resistance materials for electrical preheating of exhaust cleaning systems in Diesel and two-stroke systems.

The subject of the invention is described in greater detail in the following examples.

15    **DETAILED DESCRIPTION**

(Aluchrom ISE, Hf3 and Hf4 represent comparative alloys and Aluchrom Hf1 and Hf2 are the subject of the present invention).

## SECOND SUBSTITUTE SPECIFICATION

## Chemical compositions

Element/ Mass %	Aluchro ISE	Aluchrom Hf 1	Aluchrom Hf 2	Aluchrom Hf 3	Aluchrom Hf 4
Cr	20,45	17,25	18,20	21,05	20,15
NI	0,19	0,14	0,16	0,17	0,16
Mn	0,25	0,28	0,15	0,11	0,21
SI	0,43	0,54	0,29	0,30	0,22
TI	0,01	<0,01	<0,01	<0,01	0,01
Cu	0,03	0,05	0,02	0,03	0,07
S	0,002	0,002	0,002	0,002	0,002
P	0,011	0,009	0,013	0,009	0,012
Al	5,27	2,78	3,30	5,36	5,70
Mg	0,008	0,004	0,009	0,009	0,009
Zr	0,003	0,05	0,01	0,02	0,05
V	0,04	0,05	0,03	0,04	0,03
C	0,006	0,032	0,023	0,051	0,023
N	0,004	0,005	0,004	0,002	0,005
Hf	--	0,04	0,05	0,03	0,05
Y Cer MM (Ce, LA, Nd)	-- 0,015	0,03 --	0,05 --	<0,01 --	0,06

5

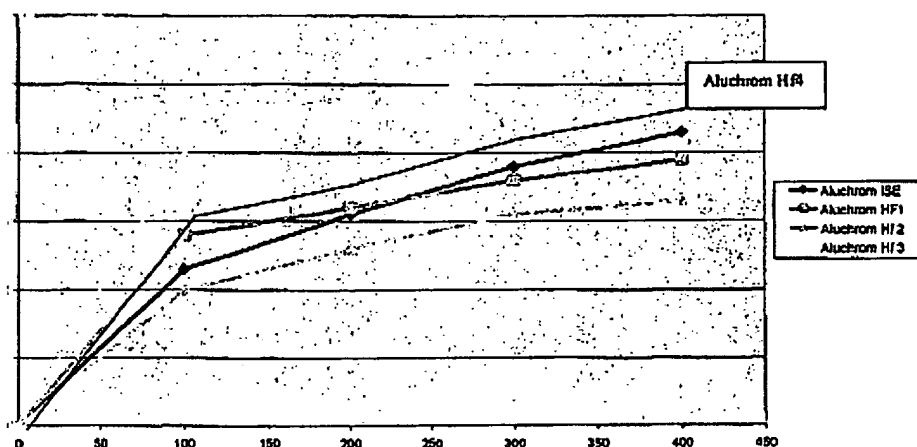
The examples in accordance with the invention were produced by melting in the electric arc furnace, continuous casting or ingot casting, hot rolling to a thickness of about 3mm, with intermediate annealing at end thicknesses of 0.02 to 0.05 and cold rolling on a 20 roller scaffold.

10

## SECOND SUBSTITUTE SPECIFICATION

## Oxidation test

Weight change at 1100°C, foil thickness 50  $\mu$



5    ↑ Weight change %                      Exposure time in h

As the examples show, besides the Al content, the exact tuning of the oxygen affine reactive elements is of predominant importance. For instance, the alloys according to the present invention, Aluchrom Hf1 and Aluchrom Hf2, in spite of their comparatively low Al-content of around 3%, show an extremely good oxidation resistance, which is similar to the comparative alloys Aluchrom ISE and Aluchrom Hf4. By comparison, Aluchrom Hf3, in spite of its high Al- content of 5.36%, has lower values which can be attributed to the Y content being too low. In this instance therefore additions of Y or Cerium mischmetal result in a markedly improved oxidation resistance. (compare Aluchrom ISE and Aluchrom Hf4).

15

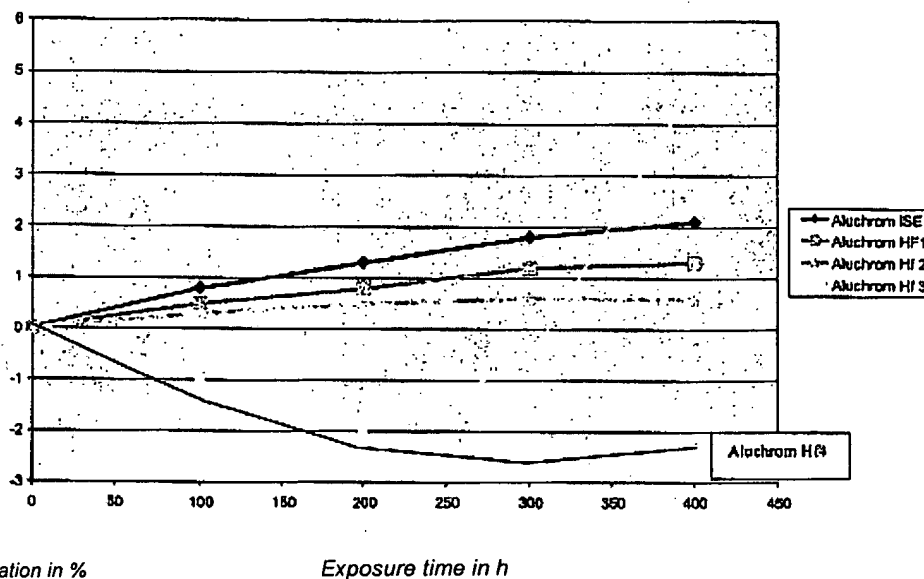
A further important aspect for the construction of metallic catalytic converter substrates for Diesel engines and two-stroke engines is the dimensional stability of the foil during the useful life of the foil. A respective characteristic feature in this regard is the linear deformation which should, if possible, not exceed 4 %.

20

## SECOND SUBSTITUTE SPECIFICATION

## Dimensional Stability

5

Linear deformation at 1100°C, 50  $\mu$  foil thickness

↑ Linear deformation in %

Exposure time in h

This also shows that the alloys in accordance with the present invention, Aluchrom Hf1 and Aluchrom Hf2, having an Al content of around 3 %, achieve a dimensional stability of < 4% as do the comparative alloys Aluchrom ISE and Aluchrom Hf4 having an Al content of > 5%. Also in this case, in spite of their comparatively high Al content of 5.36 % but too low a Y content, the comparative alloy Aluchrom Hf3 does not meet the requirements, since the linear deformation after 400 h, being about 5 %, is clearly too great.

15

Thus it is surprisingly found that with a suitable tuning of the oxygen-affine reactive elements, even where Al contents clearly below 5 % are present, a dimensional stability necessary for the production of metallic catalytic converters can be achieved.

## SECOND SUBSTITUTE SPECIFICATION

A cost-effective production, based on the comparatively low Al contents, by way of ingot casting, continuous casting or even strip casting whilst observing the application-specific parameters is thus achieved.